ALUMINUM NITRIDE MATERIAL HONEYCOMB FILTER

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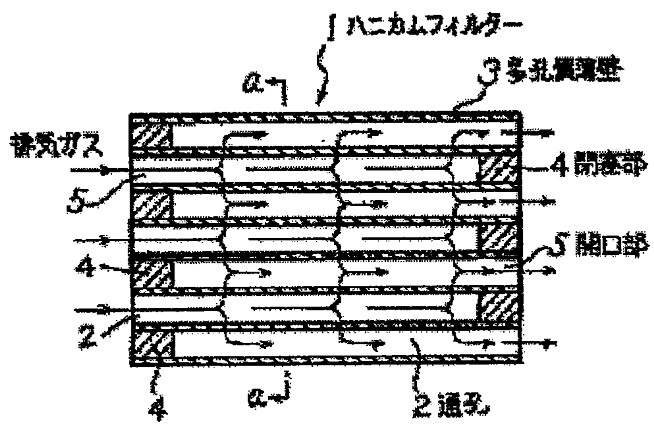
Abstract of **JP6327921**

PURPOSE:To provide the honeycomb filter which is capable of capturing suspended particulates such as carbon particles, unburned mists incorporated in the exhaust gas of an automobile engine and hardly causes fracture by high temp. at the time of regenerating the filter by heating and burning the captured suspended particulates and capable of reusing repeatedly over a long period of time. CONSTITUTION:This filter is composed of the honeycomb structure which is provided with numerous vent holes 2 opened at an end and clogged at the other end and arranged alternately with the opening part 5 and the clogging part 4 of each vent hole 2 at the ends, and the honeycomb structure is formed with the porous aluminum nitride having the porosity of 15-65vol.% or the aluminum nitride material honeycomb filter whose surface is coated with silicon carbide.



PATENT ABSTRACTS OF JAPAN

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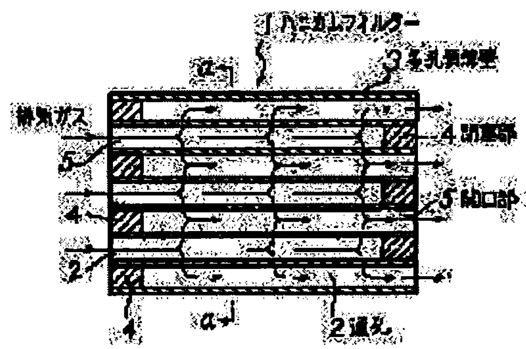
(54) ALUMINUM NITRIDE MATERIAL HONEYCOMB FILTER

(57)Abstract:
PURPOSE: To provide the honeycomb filter which is capable of capturing suspended particulates such as carbon particles, unburned mists incorporated in the exhaust gas of an automobile engine and hardly causes fracture by high temp. at the time of regenerating the filter by heating and burning the captured suspended particulates and capable of reusing repeatedly over a long period of time.
CONSTITUTION: This filter is composed of the honeycomb structure which is provided with numerous vent holes 2 opened at an end and clogged at the other end and arranged alternately with the opening part 5 and the clogging part 4 of each vent hole 2 at the ends, and the honeycomb structure is formed with the porous aluminum nitride having the porosity of 15-65vol.% or the aluminum nitride material honeycomb filter whose surface is coated with silicon carbide.



CLAIMS

[Claim(s)]
[Claim 1]Have a through-hole of a large number which carried out the opening of the one end, and blockaded the other end, and it consists of a honeycomb structured body arranged so that an opening and an occlusion part of each through-hole may become alternate at both ends, A nature honeycomb filter of alumimium nitride in which the honeycomb structured body concerned is formed by porous aluminum nitride of the porosity 15 - 65 volume %.
[Claim 2]The nature honeycomb filter of alumimium nitride according to claim 1, wherein an average pore size of porous aluminum nitride is in within the limits which is 0.01-100 micrometers.
[Claim 3]The nature honeycomb filter of alumimium nitride according to claim 1 or 2, wherein thickness of a porosity thin wall of porous aluminum nitride which divides each through-hole of a honeycomb structured body is 0.2-0.7 mm.
[Claim 4]The nature honeycomb filter of alumimium nitride according to any one of claims 1 to 3 covering 0.01-10-micrometer-thick silicon carbide on the surface of porous aluminum nitride.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to the honeycomb filter for catching a carbon particle, unburned mist, dust, etc. which are contained in the exhaust gas from an automobile engine, etc.
[0002]
[Description of the Prior Art]In recent years, carbon dioxide, nitrogen oxides, a black smoke, etc. which are contained in the exhaust gas of a car are made into a problem as a causative agent of air pollution as part of earth environment protection, and the effluent control is becoming severe gradually. About floating fine particles contained mostly especially in the emission gas of a diesel power plant among the substances which have been the targets of effluent control, such as a carbon particle, unburned mist, and dust, it considers catching with the filter arranged in a muffler.
[0003]For example, the honeycomb filter which consists of a honeycomb structured body provided with the through-hole of a large number blockaded at at least one place is arranged in a muffler, Since pressure loss will become large if a floating fine particle is caught and the caught floating fine particle deposits to some extent while the exhaust gas included in a through-hole flows through the fine pores of the thin wall of the porosity which divides each through-hole, With a heater, heating calcination is carried out momentarily, the floating fine particle which deposited is removed, and the honeycomb filter it enabled it to reproduce in the state where there is no precipitate is proposed.
[0004]In order not to reduce engine combustor efficiency, while the filter material itself consists of a substance of the porosity excellent in breathability, in order that this honeycomb filter may carry out heating removal of the floating fine particle which deposited and may reproduce a filter, It is required to have the heat resistance of not less than 1000 ** and the outstanding thermal shock resistance which bears a thermal excursion. Therefore, promising ** of the silicon carbide (SiC) which was excellent in porous ceramics especially cordierite with a small coefficient of thermal expansion, or thermal conductivity as a filter material is carried out.
[0005]However, the honeycomb filter which consists of cordierites has a risk of fusing according to the elevated temperature at the time of calcinating the caught floating fine particle and reproducing a filter, or being destroyed. Temperature distribution arose inside the honeycomb structured body at the elevated temperature when calcinating the caught floating fine particle and reproducing a filter also in the case of the honeycomb filter which is excellent in heat resistance and consists of SiC with high thermal conductivity, and there was a fault which will be destroyed by the heat stress generated in that case if heat regenerating is repeated.
[0006]In order to prevent destruction of a honeycomb filter, when temperature of heating calcination is made low, since removal of the floating fine particle which deposited is insufficient, the pressure loss after reproduction does not become small, but it stops fully functioning as a filter. Since pressure loss becomes extremely large by 1 time or two reproduction and it stops already recovering in the state with the performance near origin as a filter, it becomes impossible for example, to continue use further after reproduction in heating calcination of 1000 ** or less.
[0007]
[Problem(s) to be Solved by the Invention]The carbon particle by which this invention is contained in the exhaust gas of an automobile engine in view of this conventional situation,

Floating fine particles, such as unburned mist and dust, can be caught, and it does not destroy with the heat stress by the elevated temperature at the time of carrying out heating calcination of the caught floating fine particle, and reproducing a filter, and aims at providing the honeycomb filter which can carry out repetition reproduction use over a long period of time.

[0008]

[Means for Solving the Problem]In order to attain the above-mentioned purpose, a honeycomb filter which this invention provides, It has a through-hole of a large number which carried out the opening of the one end, and blockaded the other end, and consists of a honeycomb structured body arranged so that an opening and an occlusion part of each through-hole may become alternate at both ends, and the honeycomb structured body concerned is formed by porous aluminum nitride of the porosity 15 - 65 volume %.

[0009]

[Function]In the honeycomb filter of this invention, alumimium nitride (AlN) is used as a honeycomb structured body. AlN has the heat resistance of about 1700 **, and is one of the materials with the highest thermal conductivity in ceramics. For example, the thermal conductivity of precise AlN also reaches 120 W/mK to the thermal conductivity of general precise SiC being about 63 W/mK. Although the heat exchanger of the honeycomb structure which consists of precise AlN using this feature is also considered, it must porosity-ize so that exhaust gas etc. may penetrate, in using AlN as a filter.

[0010]However, if AlN is porosity-ized, the fall of thermal shock resistance will arise with decline in thermal conductivity as a material, and it will become easy to destroy according to the elevated temperature at the time of filter regeneration. Then, by adjusting the porosity of porous AlN to 15 - 65 volume % in this invention, A filter function, thermal conductivity, and thermal shock resistance can be reconciled, and the honeycomb filter which is not destroyed according to the elevated temperature at the time of the filter regeneration in which the caught floating fine particle carries out heating calcination, either can be obtained.

[0011]That is, by less than 15 volume %, the porosity of AlN will break according to the elevated temperature at the time of heating calcination of the floating fine particle caught due to decline in thermal conductivity, if pressure loss becomes large, and does not exhibit the function as a filter but exceeds 65 volume % conversely. However, the honeycomb structured body formed by the porosity AlN adjusted to the porosity of the range of 15 - 65 volume % of this invention, Since the temperature distribution inside a honeycomb structured body can be small suppressed for high thermal conductivity even if exposed to an elevated temperature while it has the outstanding filter function, even if it repeats reproduction of the filter by heating calcination of the caught floating fine particle, it does not destroy with heat stress.

[0012]A honeycomb filter is the honeycomb structured body provided with many through-holes, and it has the structure which blockaded each through-hole at at least one place so that the exhaust gas included in each through-hole may penetrate the porosity thin wall which divides each through-hole. Like [in order to make a filtration usable area into the maximum] the nature honeycomb filter 1 of AlN of this invention shown in drawing 1 and drawing 2, It is the honeycomb structured body provided with the through-hole 2 of a large number which carried out the opening of the one end, and blockaded the other end, and it is preferred to arrange so that the opening 5 and the occlusion part 4 of each through-hole 2 may become alternate at the both ends of the honeycomb structured body.

[0013]Although the exhaust gas of a car enters in the through-hole 2 from the opening 5 of the end of the honeycomb filter 1 and is discharged out of a filter from the opening 5 of the through-hole 2 which passes the fine pores of the porosity thin wall 3 which consists of the porosity AlN which divides each through-hole 2, and adjoins, When passing the fine pores of the porosity thin wall 3, floating fine particles contained in exhaust gas, such as a carbon particle, unburned mist, and dust, are caught. Therefore, according to the size of the floating fine particle which is contained in exhaust gas and which should be caught, within the limits of 0.01-100 micrometers sets up preferably the average pore size of AlN of the porosity which constitutes the honeycomb filter 1 within the limits of 5-50 micrometers.

[0014]When it is too thin, intensity becomes less enough [the thickness of the porosity thin wall 3 which divides each through-hole 2 of the honeycomb filter 1], and since it will interfere with the penetration of exhaust gas if it is too thick, its range of 0.2-0.7 micrometer is preferred. As long as the occlusion part 4 which blockades the through-hole 2 is a material which bears the

calcination temperature of the caught floating fine particle, the restriction in particular may not have it, for example, it may be SiC etc. However, as for the occlusion part 4, it is desirable on consistency of a coefficient of thermal expansion or thermal conductivity, or manufacture that it is the same porosity AlN as a honeycomb structured body, and in that case, in order to bar the penetration of exhaust gas, it is required [the thickness (shaft-orientations length) of the occlusion part 4 of the porosity ALN] for it not less than 3 mm.

[0015]What is necessary is just to reduce sintering temperature rather than the case where precise AlN is manufactured, in order to manufacture the porosity AlN. For example, after mixing AlN powder and sintering aid powder, such as Y_2O_3 and CaO, and fabricating this end of precursor powder, in precise AlN, by the porosity AlN, it sinters at the temperature below about 1800 ** to sintering at about 1800-1900 ** in a nitrogen gas atmosphere. Carbon, an organic blowing agent, etc. are beforehand mixed during the end of precursor powder, and AlN can be made to porosity-ize also by making it disappear, while sintering these. Control of porosity can be attained by control of content, such as sintering temperature or an organic blowing agent.

[0016]The process of the honeycomb structured body which consists of this porosity AlN fabricates the AlN powder which mixed the sintering aid to honeycomb shape by an extrusion method, injection molding process, etc., and should just sinter this Plastic solid like the above. After manufacture of an occlusion part fabricates a honeycomb structured body or sinters it, it may blockade each through-hole of the both ends alternately, and, It is also possible to form an occlusion part in one with a honeycomb structured body by also fabricating the occlusion part which blockades each through-hole simultaneously with shaping of a honeycomb structured body by injection molding to a metallic mold, and sintering simultaneously succeedingly.

[0017]As one desirable mode of the honeycomb filter of this invention, the honeycomb filter which covered 0.01-10-micrometer-thick silicon carbide (SiC) is shown in the surface of the porosity AlN which forms a honeycomb filter. Since the oxidation resistance in an elevated temperature improves by covering 0.01 micrometers or more-thick SiC to the skeletal surface and fine-pores internal surface of the porosity AlN, can set up the calcination temperature of the caught floating fine particle more highly, but. If the thickness of SiC exceeds 10 micrometers, thermal conductivity will fall by a SiC layer and heat stress destruction will be promoted conversely.

[0018]If the temperature of AlN generally exceeds 1000 **, in order for oxidation to become intense, and for AlN to oxidize and to generate $aluminum_2O_3$, as a result of the thermal conductivity of the generation portion of $aluminum_2O_3$ falling rather than other portions and a temperature gradient's arising, it becomes easy to cause heat stress destruction. Since according to the desirable mode of this invention oxidation of AlN can be prevented and generation of $aluminum_2O_3$ can be lost by covering SiC on the AlN surface, Since the calcination temperature of the floating fine particle caught rather than the case where SiC is not covered can be set more as an elevated temperature and the survival rate of the floating fine particle after calcination falls as a result, the pressure loss at the time of a honeycomb filter reuse becomes small.

[0019]The coating method of SiC to a honeycomb filter, The method on which SiC is made to laminate is shown in the AlN skeletal surface, the fine-pores inner surface, and the occlusion part surface of a porosity thin wall, introducing material gas from the opening of a honeycomb filter, and making it discharge from the opening of an opposite hand through a porosity thin wall with the chemicals gaseous phase infiltration process which is a kind of a CVD method. In that case, it is necessary to optimize conditions, such as material gas concentration, reaction temperature, and reaction pressure, so that uniform SiC may be deposited over the whole porosity AlN.

[0020]

[Example]

To AlN powder with example 1 mean particle diameter of 0.8 micrometer, Y_2O_3 powder was added 0.6% of the weight as a sintering aid, and what added organic blowing agent AZOJI carvone amide to this powder mixture simple substance and this powder mixture 0.2% of the weight was kneaded with optimum dose of organic binders. The Plastic solid of the honeycomb filter shape where the both ends of the through-hole were obtained by blockading alternately with the same

paste as the obtained paste was fabricated to honeycomb shape by extrusion molding and also it was shown in drawing 1 and drawing 2 was sintered at the sintering temperature of 1680-1800 ** in a nitrogen gas atmosphere for 2 hours.

[0021]The honeycomb filter 1 of each obtained quality of AlN, The thickness of 0.4 micrometer and the occlusion part 4 of the thickness of the porosity thin wall 3 which is provided with the through-hole 2 of a large number which carried out the opening of the one end, and blockaded the other end, has the structure arranged so that the opening 5 and the occlusion part 4 of each through-hole 2 may become alternate at the both ends, and consists of the porosity AlN is 5.0 mm.

The filtration usable area was 23-m^2.

It asked for the porosity of each honeycomb filter 1, and the mean bore diameter of fine pores was measured and it was shown in Table 1.

[0022]For comparison, a proper quantity of SiO_2 powder and B powder were added as a sintering aid to SiC powder with a mean particle diameter of 0.5 micrometer, and ultrasonic mixing was carried out in ethanol. This powder mixture was fabricated in the same honeycomb filter shape as the above, and each Plastic solid was sintered at the sintering temperature of 1700-1800 ** in argon gas atmosphere for 3 hours. The honeycomb filter which consists of each acquired porosity SiC had the same structure and size as the above-mentioned nature honeycomb filter of AlN, and the filtration usable area of it was also the same as that of 23-m^2.

[0023]These honeycomb filters are attached to the exhaust gas purifying facility of a diesel power plant, After operating by 900 rpm of engine speed values for 1 hour, the filter regeneration process which vanishes the floating fine particle caught by making 1000 ** heat a honeycomb filter with the attached heater was repeated a maximum of 10 times. The routing counter until measure the pressure loss after the 1st filter regeneration process, and it evaluates a catching function, and it observes a honeycomb filter for 1 time of every filter regeneration process and destruction and a crack arise was counted. These test results were combined with Table 1, and were shown.

[0024]

[Table 1]

sintering temperature Porosity Average fine-pores pressure Power Loss Sample material to ****** . Number of diameter (micrometer) (mmHg) evaluation processes of nature (**) (volume %) (time) 1* AlN 1680 75.23 106.9 3O1 2* AlN 1700 65.02 80.0 8O1 3 AlN 1680 52.69. 45.7 16O7 4 AlN 1700. 44.36 29.1 21O9 5 AlN. 1720 36.33 15.3 25 O. 10 (it does not destroy) 6 AlN 1740. 28.85 12.3 29O10 (it does not destroy). 7 AlN 1760 15.01 9.1. 33 O 10 (it does not destroy) 8* AlN. 1780 10.21 5.9 39 x. 10 (it does not destroy) 9* AlN 1820. 3.45 2.3 66 x 10 (it does not destroy) 10*. AlN 1840 0.05 0.1 450. x10 (it does not destroy) 11* SiC 1700 55.33 45.0 13 O 112* SiC 1750 45.01 27.3 21 O 113*SiC 1800 10.36 6.6 The sample which attached * in 39 x 3 (notes) front is a comparative example. The samples 1 and 2 are the examples which formed the porosity AlN by addition of the organic blowing agent.

[0025]As opposed to destruction having been accepted in part by each at the filter regeneration process up to 3 times as for the honeycomb filter which consists of the porosity SiC, as shown in the above-mentioned table 1, Since the honeycomb filter which consists of the porosity AlN which adjusted the porosity of this invention had high heat dissipation nature, even if heated to the calcination temperature up to 1000 **, the damage by heat stress was not able to occur, but it was able to repeat 7 times or more of filter regeneration processes.

[0026]Use as a substrate the honeycomb filter of the sample 5 shown in Table 1 of example 2 Example 1, and with the following material gas and the CVD method of a film formation condition. Material gas was passed through each through-hole from the end side of a honeycomb filter, and the SiC-coating layer was formed in the AlN skeletal surface, the fine-pores inner surface, and the occlusion part surface of a honeycomb structured body at a thickness of about 1 micrometer, making it discharge from an opposite hand.

[0027]Material gas and a film formation condition: SiCl flow 0.5 l/minCH_4 flow 0.2 l/minH_2 flow 3.0 l/min covering temperature 1450 ** gas pressure 0.2 Torr covering time 10 hours [0028] Porosity and an average pore size were measured about the honeycomb filter which consists of a honeycomb structured body of the acquired porosity AlN which carried out SiC coating. This honeycomb filter is attached to the exhaust gas purifying facility of the same diesel power plant

as Example 1, After operating by the same engine speed value as Example 1 for 24 hours and catching a floating fine particle, heating calcination was carried out with the calcination temperature of 1000 **, 1200 **, and 1300 **, respectively, and the filter was reproduced. The pressure loss before and behind the filter regeneration in each calcination temperature was measured, and the result was shown in Table 2. For comparison, the examination with the same said of the AlN honeycomb filter of the sample 5 which does not cover SiC was done, and the result was combined with Table 2 and shown.

[0029]

[Table 2]

SiC Porosity Average fine pores Diameter (micrometer) (**) calcination forward calcination backward 5-1 Nothing 36.33 15.3 1000 60 30 5-2 Nothing 36.33 15.3 1200. [of a calcination temperature pressure loss (mmHg) sample enveloping layer (volume %)] 61 Destroy in part. Those with 5-3 36.11 13.2 1000 61 Those with 305-4 36.10 13.3 1200 60 Those with 55-5 35.99 13.0 1300 60 2[0030]Although breakage occurred in the honeycomb filter which consists of the porosity AlN which has not covered SiC with the calcination temperature of 1200 ** at the time of filter regeneration, in the honeycomb filter which covered SiC, even the calcination temperature of 1300 ** did not have breakage and was healthy. If the pressure loss after filter regeneration becomes small and is calcinated at the temperature of not less than 1200 ** as calcination temperature becomes high, it turns out that it is possible to return the state of a filter to the state before the catching start of a floating fine particle mostly.

[0031]

[Effect of the Invention]The carbon particle which is contained in the exhaust gas of an automobile engine according to this invention, It does not destroy with the heat stress by the elevated temperature at the time of being able to catch floating fine particles, such as unburned mist and dust, carrying out heating calcination of the caught floating fine particle, and reproducing a filter, either, The honeycomb filter which consists of a honeycomb structured body of the porosity AlN which can carry out reproduction use by repetition heating calcination can be provided.

[0032]Especially the honeycomb filter that covered SiC to the honeycomb structured body of the porosity AlN, Since oxidation on the surface of AlN can be prevented, the calcination temperature over 1000 ** can also be borne, therefore it becomes possible to reduce further the pressure loss after the filter regeneration by heating calcination, and to return it even near the initial state before use, and use further stable over the long period of time can be performed.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]It is a sectional view of an outline showing one example of the nature honeycomb filter of alumimium nitride of this invention.
[Drawing 2]It is a sectional view of the outline of the nature honeycomb filter of alumimium nitride of this invention which met the a-a line of drawing 1.
[Description of Notations]
1 Honeycomb filter
2 Through-hole
3 Porosity thin wall
4 Occlusion part
5 Opening

[Translation done.]

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審査請求　未請求　請求項の数４　ＦＤ　（全　５　頁）

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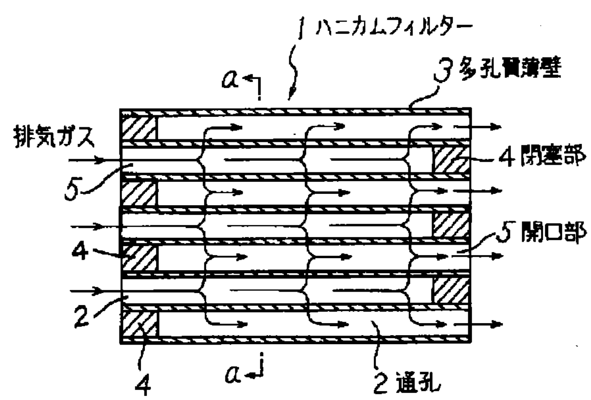
(54)【発明の名称】　窒化アルミニウム質ハニカムフィルター

(57)【要約】

【目的】　自動車エンジンの排気ガスに含まれるカーボン粒子、未燃焼ミスト、粉塵等の浮遊微粒子を捕集でき、捕集した浮遊微粒子を加熱焼成してフィルターを再生する際の高温によって破壊することがなく、長期にわたり繰り返し再生使用することが可能なハニカムフィルターを提供する。

【構成】　一端を開口し且つ他端を閉塞した多数の通孔２を備え、両端で各通孔２の開口部５と閉塞部４とが互い違いになるように配置されたハニカム構造体からなり、当該ハニカム構造体が気孔率１５～６５体積％の多孔質窒化アルミニウムで形成されているか、又はその表面に炭化ケイ素を被覆してなる窒化アルミニウム質ハニカムフィルター。



【特許請求の範囲】

【請求項１】　一端を開口し且つ他端を閉塞した多数の通孔を備え、両端で各通孔の開口部と閉塞部とが互い違いになるように配置されたハニカム構造体からなり、当該ハニカム構造体が気孔率１５～６５体積％の多孔質窒化アルミニウムで形成されている窒化アルミニウム質ハニカムフィルター。

【請求項２】　多孔質窒化アルミニウムの平均細孔径が０．０１～１００μｍの範囲内にあることを特徴とする、請求項１に記載の窒化アルミニウム質ハニカムフィルター。

【請求項３】　ハニカム構造体の各通孔を区画する多孔質窒化アルミニウムの多孔質薄壁の厚さが０．２～０．７ｍｍであることを特徴とする、請求項１又は２に記載の窒化アルミニウム質ハニカムフィルター。

【請求項４】　多孔質窒化アルミニウムの表面に厚さ０．０１～１０μｍの炭化ケイ素を被覆したことを特徴とする、請求項１～３のいずれかに記載の窒化アルミニウム質ハニカムフィルター。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、自動車エンジンからの排気ガス等に含まれるカーボン粒子、未燃焼ミスト、粉塵等を捕集するためのハニカムフィルターに関する。

【０００２】

【従来の技術】近年、地球環境保護の一環として、自動車の排気ガス中に含まれる二酸化炭素や窒素酸化物、黒煙等が大気汚染の原因物質として問題とされ、その排出規制が次第に厳しくなっている。排出規制の対象となっている物質のうち、特にディーゼルエンジンの排出ガス中に多く含まれるカーボン粒子、未燃焼ミスト、粉塵等の浮遊微粒子については、マフラー中に配置するフィルターによって捕集することが考えられている。

【０００３】例えば、少なくとも１カ所で閉塞された多数の通孔を備えたハニカム構造体からなるハニカムフィルターをマフラー中に配置し、通孔に入った排気ガスが各通孔を区画する多孔質の薄壁の細孔を通って流れる間に浮遊微粒子を捕集し、捕集された浮遊微粒子がある程度沈積すると圧力損失が大きくなるので、沈着した浮遊微粒子をヒーターで瞬間的に加熱焼成して取り除き、沈着物のない状態に再生できるようにしたハニカムフィルターが提案されている。

【０００４】かかるハニカムフィルターは、エンジンの燃焼効率を低下させないためフィルター材料自体が通気性に優れた多孔質の物質からなると同時に、沈着した浮遊微粒子を加熱除去してフィルターを再生するため、１０００℃以上の耐熱性と熱サイクルに耐える優れた耐熱衝撃性を備えることが必要である。そのため、フィルター材料としては多孔質のセラミックス、特に熱膨張係数の小さいコーディエライトや熱伝導率の優れた炭化ケイ素（ＳｉＣ）が有望視されている。

【０００５】しかし、コーディエライトからなるハニカムフィルターは、捕集した浮遊微粒子を焼成してフィルターを再生する際の高温により溶融し又は破壊される危険がある。又、耐熱性に優れ且つ熱伝導率の高いＳｉＣからなるハニカムフィルターの場合でも、捕集した浮遊微粒子を焼成してフィルターを再生する時の高温でハニカム構造体内部に温度分布が生じ、その際に発生する熱応力によって、加熱再生を繰り返すと破壊される欠点があった。

【０００６】又、ハニカムフィルターの破壊を防ぐため加熱焼成の温度を低くすると、沈着した浮遊微粒子の除去が不十分なため再生後の圧力損失が小さくならず、フィルターとして充分に機能しなくなる。例えば、１０００℃以下の加熱焼成では、１回又は２回の再生で圧力損失が極端に大きくなり、もはやフィルターとしての性能が元に近い状態に回復しなくなるため、再生後更に使用を続けることが出来なくなる。

【０００７】

【発明が解決しようとする課題】本発明は、かかる従来の事情に鑑み、自動車エンジンの排気ガス中に含まれるカーボン粒子、未燃焼ミスト、粉塵等の浮遊微粒子を捕集でき、捕集した浮遊微粒子を加熱焼成してフィルターを再生する際の高温による熱応力によって破壊することがなく、長期にわたり繰り返し再生使用することが可能なハニカムフィルターを提供することを目的とする。

【０００８】

【課題を解決するための手段】上記目的を達成するため、本発明が提供するハニカムフィルターは、一端を開口し且つ他端を閉塞した多数の通孔を備え、両端で各通孔の開口部と閉塞部とが互い違いになるように配置されたハニカム構造体からなり、当該ハニカム構造体が気孔率１５～６５体積％の多孔質窒化アルミニウムで形成されていることを特徴とするものである。

【０００９】

【作用】本発明のハニカムフィルターにおいては、ハニカム構造体として窒化アルミニウム（ＡｌＮ）を用いる。ＡｌＮは約１７００℃の耐熱性を持ち、且つセラミックスの中では最も熱伝導率が高い材料の一つである。例えば、一般的な緻密なＳｉＣの熱伝導率が約６３Ｗ／ｍＫであるのに対して、緻密なＡｌＮの熱伝導率は１２０Ｗ／ｍＫにも達する。この特徴を利用して緻密なＡｌＮからなるハニカム構造の熱交換器も考えられているが、ＡｌＮをフィルターとして用いる場合には排気ガス等が透過するように多孔質化しなければならない。

【００１０】しかし、ＡｌＮを多孔質化すると、材料として熱伝導率の低下と共に耐熱衝撃性の低下が生じ、フィルター再生時の高温により破壊し易くなる。そこで本発明では、多孔質のＡｌＮの気孔率を１５～６５体積％に調整することによって、フィルター機能と熱伝導率並

びに耐熱衝撃性とを両立させ、捕集した浮遊微粒子の加熱焼成するフィルター再生時の高温によっても破壊しないハニカムフィルターを得ることが出来たものである。

【0011】即ち、ＡｌＮの気孔率が１５体積％未満では圧力損失が大きくなり、フィルターとしての機能を発揮せず、逆に６５体積％を越えると熱伝導率の低下により、捕集した浮遊微粒子の加熱焼成時の高温により破壊する。しかし、本発明の１５～６５体積％の範囲の気孔率に調整した多孔質ＡｌＮで形成されたハニカム構造体は、優れたフィルター機能を持つと同時に、高温にさらされても高い熱伝導率のためハニカム構造体内部の温度分布を小さく抑えることが出来るので、捕集した浮遊微粒子の加熱焼成によるフィルターの再生を繰り返しても熱応力によって破壊することがない。

【0012】ハニカムフィルターは多数の通孔を備えたハニカム構造体であり、各通孔に入った排気ガスが各通孔を区画する多孔質薄壁を透過するように、各通孔を少なくとも１カ所で閉塞した構造を有する。濾過有効面積を最大にするためには、図１及び図２に示す本発明のＡｌＮ質ハニカムフィルター１のように、一端を開口し且つ他端を閉塞した多数の通孔２を備えたハニカム構造体であり、そのハニカム構造体の両端で各通孔２の開口部５と閉塞部４とが互い違いになるように配置することが好ましい。

【0013】自動車の排気ガスは、ハニカムフィルター１の一端の開口部５から通孔２内に入り、各通孔２を区画する多孔質ＡｌＮからなる多孔質薄壁３の細孔を通過して隣接する通孔２の開口部５からフィルター外に排出されるが、多孔質薄壁３の細孔を通過する際に排気ガス中に含まれるカーボン粒子、未燃焼ミスト、粉塵等の浮遊微粒子が捕集される。そのため、ハニカムフィルター１を構成する多孔質のＡｌＮの平均細孔径は、排気ガスに含まれる捕集すべき浮遊微粒子のサイズに応じて０．０１～１００μmの範囲内、好ましくは５～５０μmの範囲内で設定する。

【0014】又、ハニカムフィルター１の各通孔２を区画する多孔質薄壁３の厚さは、薄過ぎると強度が充分でなくなり且つ厚過ぎると排気ガスの透過に支障を来すので、０．２～０．７μmの範囲が好ましい。更に、通孔２を閉塞する閉塞部４は、捕集した浮遊微粒子の焼成温度に耐える材料であれば特に制限はなく、例えばＳｉＣ等であっても良い。しかし、閉塞部４はハニカム構造体と同じ多孔質ＡｌＮであることが熱膨張係数や熱伝導率の整合上又は製造上望ましく、その場合に多孔質ＡＬＮの閉塞部４の厚さ（軸方向長さ）は、排気ガスの透過を妨げるため３mm以上必要である。

【0015】多孔質ＡｌＮを製造するには、緻密なＡｌＮを製造する場合よりも焼結温度を低下させればよい。例えば、ＡｌＮ粉末とY_2O_3やＣａＯ等の焼結助剤粉末とを混合し、この原料粉末を成形した後、緻密なＡｌＮの場合は窒素ガス雰囲気中で約１８００～１９００℃で焼結するのに対して、多孔質ＡｌＮでは約１８００℃未満の温度で焼結する。又、原料粉末中に炭素や有機発泡剤等を予め混合しておき、これらを焼結中に消失させることによってもＡｌＮを多孔質化させることが出来る。尚、気孔率の制御は、焼結温度又は有機発泡剤等の含有量のコントロールにより達成することが可能である。

【0016】かかる多孔質ＡｌＮからなるハニカム構造体の製法は、焼結助剤を混合したＡｌＮ粉末を押出成形法や射出成形法等によりハニカム形状に成形し、この成形体を上記のごとく焼結すれば良い。閉塞部の製造は、ハニカム構造体を成形し又はそれを焼結した後その両端の各通孔を互い違いに閉塞しても良いし、金型への射出成形によりハニカム構造体の成形と同時に各通孔を閉塞する閉塞部も成形し、引き続いて同時に焼結することにより閉塞部をハニカム構造体と一体的に形成することも可能である。

【0017】本発明のハニカムフィルターの好ましい一態様として、ハニカムフィルターを形成する多孔質ＡｌＮの表面に厚さ０．０１～１０μmの炭化ケイ素（ＳｉＣ）を被覆したハニカムフィルターがある。多孔質ＡｌＮの骨格表面及び細孔内表面に厚さ０．０１μm以上のＳｉＣを被覆することにより高温での耐酸化性が向上するので、捕集した浮遊微粒子の焼成温度をより高く設定できるが、ＳｉＣの厚さが１０μmを越えるとＳｉＣ層により熱伝導率が低下し、逆に熱応力破壊を助長する。

【0018】一般に、ＡｌＮの温度が１０００℃を越えると酸化が激しくなり、ＡｌＮが酸化されてAl_2O_3を生成するため、Al_2O_3の生成部分の熱伝導率が他の部分よりも低下して温度勾配が生じる結果、熱応力破壊を起こし易くなる。本発明の好ましい態様によれば、ＡｌＮ表面にＳｉＣを被覆することによって、ＡｌＮの酸化を防止してAl_2O_3の生成を無くすことが出来るので、ＳｉＣを被覆しない場合よりも捕集した浮遊微粒子の焼成温度をより高温に設定でき、その結果焼成後の浮遊微粒子の残存率が低下するので、ハニカムフィルター再使用時の圧力損失が小さくなる。

【0019】ハニカムフィルターへのＳｉＣの被覆方法は、ＣＶＤ法の一種である化学気相浸透法により、ハニカムフィルターの開口部から原料ガスを導入し、多孔質薄壁を通して反対側の開口部から排出させながら、多孔質薄壁のＡｌＮ骨格表面及び細孔内部表面並びに閉塞部表面にＳｉＣを被着させる方法がある。その際、多孔質ＡｌＮの全体にわたって均一なＳｉＣを析出させるように、原料ガス濃度、反応温度、反応圧力等の条件を最適化する必要がある。

【0020】

【実施例】

<u>実施例１</u>

平均粒径０．８μmのＡｌＮ粉末に、焼結助剤としてY_2

O_3粉末を０．６重量％添加し、この混合粉末単体及びこの混合粉末に有機発泡剤アゾジカルボンアミドを０．２重量％加えたものを適量の有機バインダーと共に混練した。得られたペーストを押出成形によりハニカム形状に成形し、更に図１及び図２に示すように通孔の両端を同じペーストで互い違いに閉塞して得たハニカムフィルター形状の成形体を、窒素ガス雰囲気中にて１６８０～１８００℃の焼結温度で２時間焼結した。

【００２１】得られた各ＡｌＮ質のハニカムフィルター１は、一端を開口し且つ他端を閉塞した多数の通孔２を備え、その両端で各通孔２の開口部５と閉塞部４とが互い違いになるように配置された構造を有し、多孔質ＡｌＮからなる多孔質薄壁３の厚さは０．４μm及び閉塞部４の厚さは５．０mmであり、濾過有効面積は２３m^2であった。各ハニカムフィルター１の気孔率を求めると共に、細孔の平均内径を測定し、表１に示した。

【００２２】比較のために、平均粒径０．５μmのＳｉＣ粉末に、焼結助剤としてSiO_2粉末とＢ粉末を適量添加し、エタノール中で超音波混合した。この混合粉末＊を上記と同じハニカムフィルター形状に成形し、各成形体をアルゴンガス雰囲気中にて１７００～１８００℃の焼結温度で３時間焼結した。得られた各多孔質ＳｉＣからなるハニカムフィルターは上記ＡｌＮ質ハニカムフィルターと同じ構造及び寸法を有し、濾過有効面積も２３m^2と同一であった。

【００２３】これらのハニカムフィルターをディーゼルエンジンの排気ガス浄化装置に取り付け、エンジン回転数９００ｒｐｍにて１時間運転した後、取り付けたヒーターによりハニカムフィルターを１０００℃に加熱させることにより捕集した浮遊微粒子を消失させるフィルター再生工程を最大１０回繰り返した。１回目のフィルター再生工程後の圧力損失を測定して捕集機能の評価を行い、又１回のフィルター再生工程毎にハニカムフィルターを観察して破壊や亀裂が生じるまでの工程数を調べた。これらの試験結果を表１に併せて示した。

【００２４】

【表１】

試料	材質	焼結温度(℃)	気孔率(体積%)	平均細孔径(μm)	圧力損失 (mmHg)	圧力損失 評価	破壊までの工程数(回)
1＊	AlN	1680	75.23	106.9	3	○	1
2＊	AlN	1700	65.02	80.0	8	○	1
3	AlN	1680	52.69	45.7	16	○	7
4	AlN	1700	44.36	29.1	21	○	9
5	AlN	1720	36.33	15.3	25	○	10(破壊せず)
6	AlN	1740	28.85	12.3	29	○	10(破壊せず)
7	AlN	1760	15.01	9.1	33	○	10(破壊せず)
8＊	AlN	1780	10.21	5.9	39	×	10(破壊せず)
9＊	AlN	1820	3.45	2.3	66	×	10(破壊せず)
10＊	AlN	1840	0.05	0.1	450	×	10(破壊せず)
11＊	SiC	1700	55.33	45.0	13	○	1
12＊	SiC	1750	45.01	27.3	21	○	1
13＊	SiC	1800	10.36	6.6	39	×	3

(注) 表中の＊を付した試料は比較例である。又、試料１と２は有機発泡剤の添加により多孔質ＡｌＮを形成した例である。

【００２５】上記表１から判るように、多孔質ＳｉＣからなるハニカムフィルターは３回までのフィルター再生工程でいずれも一部に破壊が認められたのに対し、本発明の気孔率を調整した多孔質ＡｌＮからなるハニカムフィルターは高い放熱性を有するため、１０００℃までの焼成温度に加熱しても熱応力による損傷が発生せず、７回以上のフィルター再生工程を繰り返すことができた。

【００２６】<u>実施例２</u>

実施例１の表１に示した試料５のハニカムフィルターを基材とし、下記の原料ガス及び成膜条件のＣＶＤ法により、ハニカムフィルターの一端側から各通孔を通して原料ガスを流し、反対側から排出させながらハニカム構造体のＡｌＮ骨格表面及び細孔内部表面並びに閉塞部表面にＳｉＣ被覆層を約１μmの厚さに形成した。

【００２７】原料ガス及び成膜条件：

ＳｉＣｌ　流量０．５ ｌ／ｍｉｎ

CH_4　流量０．２ ｌ／ｍｉｎ

H_2　流量３．０ ｌ／ｍｉｎ

被覆温度　１４５０℃

ガス圧力　０．２ Ｔｏｒｒ

被覆時間　１０時間

【００２８】得られたＳｉＣ被覆した多孔質ＡｌＮのハニカム構造体からなるハニカムフィルターについて、気孔率と平均細孔径を測定した。又、このハニカムフィルターを実施例１と同じディーゼルエンジンの排気ガス浄化装置に取り付けて、実施例１と同様のエンジン回転数で２４時間運転して浮遊微粒子を捕集した後、それぞれ１０００℃、１２００℃、及び１３００℃の焼成温度で加熱焼成してフィルターの再生を行った。各焼成温度で

のフィルター再生前後の圧力損失を測定し、結果を表２に示した。比較のため、ＳｉＣを被覆しない試料５のＡｌＮハニカムフィルターについても同様の試験を行い、結果を表２に併せて示した。

【００２９】

【表２】

試料	ＳｉＣ被覆層	気孔率(体積%)	平均細孔径(μm)	焼成温度(℃)	圧力損失(mmHg) 焼成前	焼成後
5−1	無し	36.33	15.3	1000	60	30
5−2	無し	36.33	15.3	1200	61	一部破壊
5−3	有り	36.11	13.2	1000	61	30
5−4	有り	36.10	13.3	1200	60	5
5−5	有り	35.99	13.0	1300	60	2

【００３０】フィルター再生時の１２００℃の焼成温度により、ＳｉＣを被覆していない多孔質ＡｌＮからなるハニカムフィルターには破損が発生したが、ＳｉＣを被覆したハニカムフィルターでは１３００℃の焼成温度でも破損がなく健全であった。又、フィルター再生後の圧力損失は焼成温度が高くなるにつれて小さくなり、１２００℃以上の温度で焼成すれば、フィルターの状態をほぼ浮遊微粒子の捕集開始前の状態に戻すことが可能であることが判る。

【００３１】

【発明の効果】本発明によれば、自動車エンジンの排気ガス中に含まれるカーボン粒子、未燃焼ミスト、粉塵等の浮遊微粒子を捕集でき、捕集した浮遊微粒子を加熱焼成してフィルターを再生する際の高温による熱応力によっても破壊することがなく、繰り返し加熱焼成によって再生使用することが可能な、多孔質ＡｌＮのハニカム構造体からなるハニカムフィルターを提供することが出来る。

【００３２】特に、多孔質ＡｌＮのハニカム構造体にＳｉＣを被覆したハニカムフィルターは、ＡｌＮ表面の酸化を防ぐことが出来るので、１０００℃を越える焼成温度にも耐えることができ、従って、加熱焼成によるフィルター再生後の圧力損失を一層低下させて使用前の初期状態近くにまで戻すことが可能となり、より一層長期にわたって安定した使用が出来る。

【図面の簡単な説明】

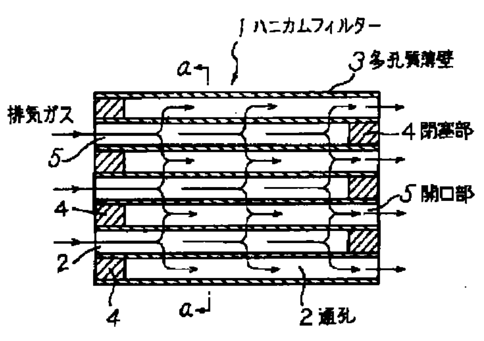
【図１】本発明の窒化アルミニウム質ハニカムフィルターの一具体例を示す概略の断面図である。

【図２】図１のａ－ａ線に沿った本発明の窒化アルミニウム質ハニカムフィルターの概略の断面図である。

【符号の説明】

1　ハニカムフィルター
2　通孔
3　多孔質薄壁
4　閉塞部
5　開口部

【図１】



【図２】